Raman spectroscopic study of the antimonate mineral bottinoite $Ni[Sb_2(OH)_{12}]\cdot 6H_2O$ and in comparison with brandholzite $Mg[Sb^{5+}{}_2(OH)_{12}]\cdot 6H_2O$

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Raman spectra of bottinoite $Ni[Sb(OH)_6]\cdot 6H_2O$ were studied, and related to the molecular structure of the mineral. An intense sharp Raman band at 618 cm^{-1} is attributed to the SbO symmetric stretching mode. The low intensity band at 735 cm^{-1} is ascribed to the SbO antisymmetric stretching vibration. Low intensity Raman bands were found at 501, 516 and 578 cm^{-1}. Four Raman bands observed at 1045, 1080, 1111 and 1163 cm^{-1} are assigned to δ SbOH deformation modes. A complex pattern resulting from the overlapping band of the water and hydroxyl units is observed. Raman bands are observed at 3223, 3228, 3368, 3291, 3458 and 3510 cm^{-1}. The first two Raman bands are assigned to water stretching vibrations. The two higher wavenumber Raman bands observed at 3466 and 3552 cm^{-1} and two infrared bands at 3434 and 3565 cm^{-1} are assigned to the stretching vibrations of the hydroxyl units. Observed Raman and infrared bands are connected with O-H…O hydrogen bonds and their lengths 2.72, 2.79, 2.86, 2.88 and 3.0 Å (Raman) and 2.73, 2.83 and 3.07 Å (infrared).

KEYWORDS: bottinoite, brandholzite, antimonate, antimonite, molecular water, Raman, infrared, spectroscopy

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INTRODUCTION

The mineral bottinoite $NiSb^{5+}_2(OH)_{12}\cdot 6H_2O$ [1] is a nickel antimony hydrated hydroxide mineral. The structure has been solved [2] and is hexagonal. Structural data and images of the structure may be obtained from the American mineralogist web site [http://crystalimpact.com/diamond/download.htm]. The $Sb(OH)_6$ and $Ni(OH)_6$ octahedra may be clearly observed. In the crystallographic structure two $Sb(OH)_6$ units are observed. The light blue-green, transparent, mineral occurs as tabular or very short prismatic crystals forming roselike aggregates; with crystals up to 0.4 mm and aggregates up to 2.5 mm in diameter. The mineral has been found in quite a number of places throughout the world [3]. The mineral bottinoite has the same structure as brandholzite $MgSb^{5+}_2(OH)_{12}\cdot 6H_2O$ [4, 5]. The mineral is also isomorphous with synthetic $Co(H_2O)_6[Sb(OH)_6]_2$ [6] and brandholzite $MgSb^{5+}_2(OH)_{12}\cdot 6H_2O$ [4, 5, 7].

In his treatise on the infrared spectra of minerals, Farmer reported the results of the infrared spectra of some synthetic antimonite minerals (see page 413 and 414 with Tables 17. XVIII and XIX) [8]. For the synthetic compound $NaSb(OH)_6$ which is an octahedral compound, infrared bands were observed at 600 and 628 cm^{-1} (very intense), 735, 775 cm^{-1} (medium intensity), and 528 and 586 cm^{-1}. Siebert researched the infrared spectra of selected synthetic antimonates [9, 10]. He assigned bands in the 528 to 775 cm^{-1} region to the stretching vibrations of SbO units; in the 1030 to 1120 cm^{-1} to the deformation modes of SbOH units and in the 3220 to 3400 cm^{-1} to the stretching bands of SbOH.

It is interesting to note that only very few papers have been published on the spectroscopy of antimonate minerals. What research has been published is related to the analysis of pigments [11-13]. Some spectroscopic studies of calcium and lead antimonates have been forthcoming [14-16]. Very few studies of related minerals/compounds such as bottinoite, brandholzite and synthetic $Co(H_2O)_6[Sb(OH)_6]_2$ have not been undertaken [17-19]. Raman spectroscopy has proven especially useful for the study of related minerals [20-31]. As part of a comprehensive study of the molecular structure of secondary minerals containing oxy-anions, formed in the oxide zone, using IR and Raman spectroscopy, we report the Raman properties of the antimonate mineral brandholzite. The spectra are related to the mineral molecular structure.

EXPERIMENTAL

Minerals

The mineral bottinoite was supplied by the mineralogical research company. The mineral originated from the Bottino mine, Italy. The chemical composition of the mineral has been published [32]. The mineral analysed as 62.6 Sb_2O_3 , 15.2% NiO and 32.9 % H_2O. The chemical analysis of the mineral depends upon its origin and may contain some As_2O_5 [3]. A Raman spectrum of bottinoite originating from the Ramsbeck mine, Dornberg, Sauerland, Germany was downloaded from the RRUFF data base.

Raman spectroscopy

The crystals of bottinoite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Further details have been published [20-31] . In the RRUFF data base [http://rruff.info/Bottinoite] a Raman spectrum of bottinoite originating from the Ramsbeck mine, Dornberg, Sauerland, Germany is shown. No band assignments were given.

IR spectroscopy

The FTIR spectrum of bottinoite was obtained with the FTIR Nicolet 740 spectrometer using the conventional KBr-disk technique. Infrared spectrum in the range 4000-400 cm^{-1} was obtained by the co-addition of 32 scans with a resolution of 2 cm^{-1} and a mirror velocity of 0.1496 cm/s. Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the OMNIC software package (Thermo Electron Corporation). Band component analysis was undertaken using the same software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly.

Band fitting of both the Raman and infrared spectra was undertaken using a Lorentz-Gauss cross-product function as spectral peak shape with the minimum number of component bands used for the fitting process which was undertaken until converged results were obtained with

minimum value of standard errors (usually lower than 2, the range for brandholzite spectra is 1.30-0.20).

RESULTS AND DISCUSSION

The Raman spectrum of the mineral bottinoite in the 400 to 800 cm^{-1} region is shown in Fig. 1. The observed central peak is distinctly asymmetric and bands may be resolved at 599, 618 and 630 cm^{-1}. Infrared bands for bottinoite were observed at 527, 600, 637, 693, 741 and 788 cm^{-1}. In the Raman spectrum of bottinoite in the RRUFF data base (spectrum not shown), a very intense band is observed at 615 cm^{-1}. Low intensity bands of bottinoite (this sample) are resolved at 501, 516 and 735 cm^{-1}. Low intensity bands for the bottinoite from the RRUFF data base were displayed at 412 and 498 cm^{-1}. A comparison may be made with the mineral brandholzite which is isomorphous with bottinoite. The Raman spectrum of brandholzite shows some complexity as well with a number of overlapping bands curve resolved at 618, 630 and 730 cm^{-1} with additional low intensity resolved bands found at 503, 526 and 578 cm^{-1}. According to Siebert [9, 10] all bands in the 500 to 800 cm^{-1} region are assignable to SbO stretching vibrations. The peaks in this spectral region of bottinoite are due to the $Sb(OH)_6^{2-}$ ionic group. The observation of multiple bands in the Raman spectrum of bottinoite provides evidence for the non-equivalence of SbO units in the bottinoite structure. In the infrared spectrum of antimony pentoxide an intense band is observed at 740 cm^{-1} and low intensity bands at ~370, 450 and 680 cm^{-1} [33]. The infrared spectrum of valentinite $(Sb_2O_3)_4$ showed bands in similar positions [33]. Farmer reported the band positions of synthetic antimonates of formula $MSbO_4$ where M is Cr, Fe, Ga or Rh with a rutile type structure [8]. As such these structures should have four Raman active bands ($A_{1g} + B_{1g} + B_{2g} + E_g$) and four infrared active bands ($A_{2u} + 3E_u$). Infrared bands were observed in the 660 to 735 cm^{-1}, 520 to 585 cm^{-1}, 285 to 375 cm^{-1} and 170 to 190 cm^{-1}. Although no assignment was given to these bands but one possible interpretation is that the first band is attributed to the antisymmetric stretching mode, the second to the symmetric stretching mode, the third to bending modes and the fourth to a lattice modes. Hence the bands of brandholzite at around 618 cm^{-1} are attributable to the $Sb(OH)_6^{2-}$ symmetric stretching modes. The observation of several bands in this spectral region supports the concept that the $Sb(OH)_6^{2-}$ units are not equivalent. Such a suggestion fits well with the crystallographic structure of bottinoite where at least two different $Sb(OH)_6^{2-}$ units are observed. In the infrared spectrum of the compound

$NaSb(OH)_6$ which has an octahedral structure, a very intense band is observed at 628 cm^{-1} with bands of lower intensity at 775 and 528 cm^{-1} [8].

The Raman spectrum of bottinoite in the 100 to 400 cm^{-1} region is displayed in Fig. 2. Raman bands are resolved at 302, 317, 336 and 361 cm^{-1}. Strong Raman bands were observed for the bottinoite sample from Germany at 300 and 331 cm^{-1} [see the spectrum in the RRUFF data base: http://rruff.info/bottinoite/display=default/]. Intense Raman bands for brandholzite are observed at 303, 318 and 340 cm^{-1}. One likely assignment of these bands for these two isomorphous minerals is to OSbO bending modes of the $Sb(OH)_6^{2-}$ units. Such an assessment fits well with the assignment of bands for $MSbO_4$ structures as reported by Farmer [8]. The observation of multiple bands in this spectral region offers support again to the concept that the non-equivalence of $Sb(OH)_6^{2-}$ units in the bottinoite structure, as is observed in the crystal structure. Other somewhat lower intensity bands are observed at 114, 125, 146, 169, 207, 235 and 254 cm^{-1}. Low intensity bands for brandholzite are observed at 115, 147, 191, 232 and 252 cm^{-1}. The bands for the two minerals are coincident. This shows the commonality of the two minerals.

The Raman spectrum of bottinoite in the 800 to 3800 cm^{-1} is shown in Fig. 3. Raman bands in this spectral region are of a very low intensity. (The scaling factor is high in Fig. 3) Two sets of bands are observed (a) in the 1000 to 1200 cm^{-1} region and (b) centred upon 1648 cm^{-1}. Four Raman bands are observed at 1045, 1080, 1111 and 1163 cm^{-1}. For the German mineral specimen, low intensity Raman bands are observed at 1031, 1061 and 1154 cm^{-1}. These bands may be compared with those observed for the mineral brandholzite where four Raman bands are observed at 1043, 1092, 1160 and 1189 cm^{-1}. These bands are assigned to δ SbOH deformation modes. Raman bands in similar positions have been observed for hydroxyls bonded to heavy metal atoms for example U-OH. The bands are attributed to the wagging of the hydroxyl units on the antimony. Siebert reported four infrared bands at 1030, 1075, 1105 and 1120 cm^{-1} for the synthetic compound $NaSb(OH)_6$. The position and number of these infrared bands for his compound is in good agreement with the position of the Raman bands of bottinoite and brandholzite. The low intensity Raman band at 1648 cm^{-1} is ascribed to the water HOH bending mode. The position of the band for liquid water is ~1630 cm^{-1}. The position of the band at 1648 cm^{-1} and infrared bands at 1632 and 1653 cm^{-1} provides evidence for the water being strongly coordinated to the Ni in the bottinoite structure.

The Raman spectrum in the 2800 to 3800 cm^{-1} region (Fig. 3) shows a complex set of overlapping bands. Bands are resolved at 3223, 3228, 3368, 3291, 3458 and 3510 cm^{-1}. In comparison, Raman bands are observed for brandholzite at 3240, 3383, 3466, 3483 and 3552 cm^{-1}, these bands are attributed to OH stretching vibrations of the OH units and water. The higher wavenumber Raman bands observed at 3458 and 3510 cm^{-1} are assigned to the stretching vibrations of the OH units. There may be inferred a hydrogen-bonding network in the crystal structure of bottinoite with corresponding O-H…O hydrogen bond lengths [34] 2.72, 2.79, 2.86, 2.88 and 3.0 Å [Raman], and 2.73, 2.83 and 3.07 Å (infrared).

CONCLUSIONS

Raman spectra of bottinoite $Ni[Sb_2(OH)_{12}]\cdot 6H_2O$ have been studied and related to the structure of the mineral. A comparison of the spectra of the mineral sample from the Bottino Mine is made with other bottinoite spectra and also with the spectra of brandholzite. Raman bands were assigned $Sb(OH)_6^{2-}$ stretching modes, δ SbOH deformation modes of the $Sb(OH)_6^{2-}$ units, OH stretching modes and water stretching and bending modes. O-H…O hydrogen bond lengths in the crystal structure of bottinoite were inferred from the Raman and infrared spectra.

Acknowledgments

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192 **References**

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List of Figures

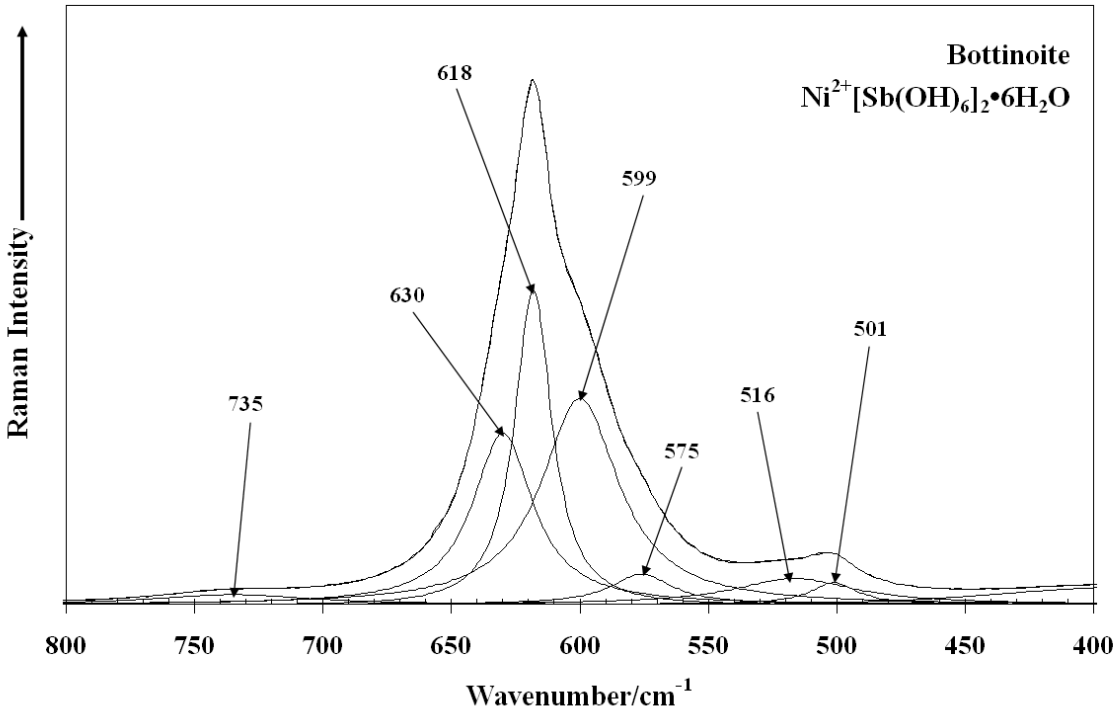

Bottinoite
$Ni^{2+}[Sb(OH)_6]_2 \cdot 6H_2O$
618
599
630
501
735
516
575
Raman Intensity
800
750
700
650
600
550
500
450
400
Wavenumber/cm^{-1}

Fig. 1

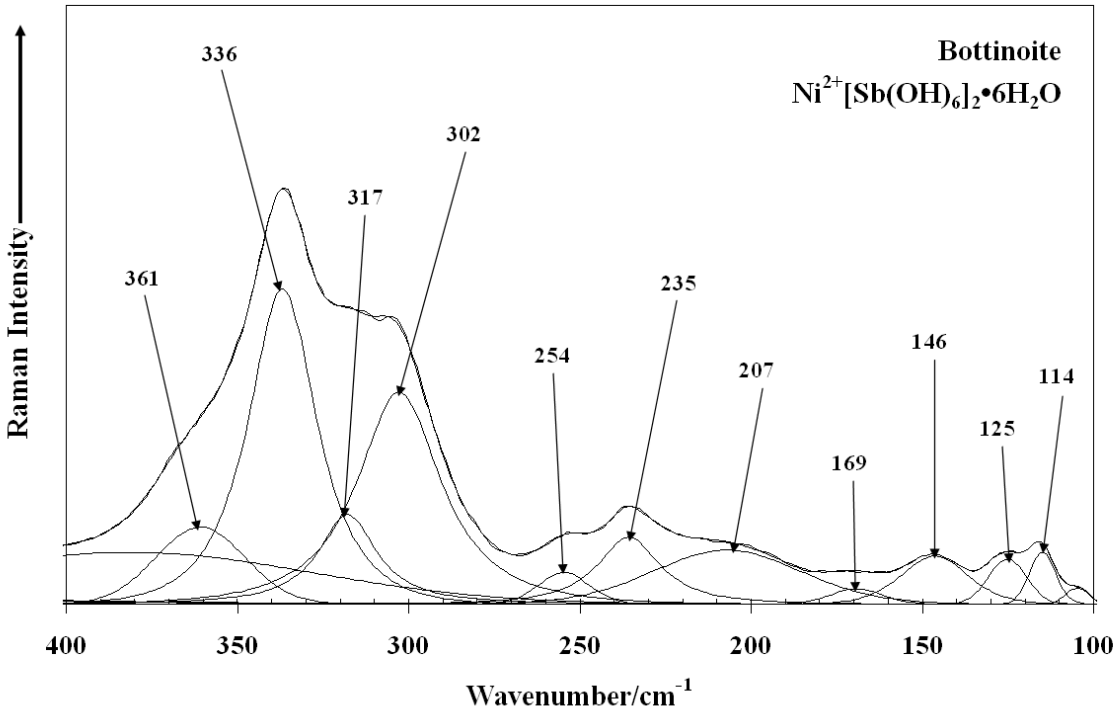
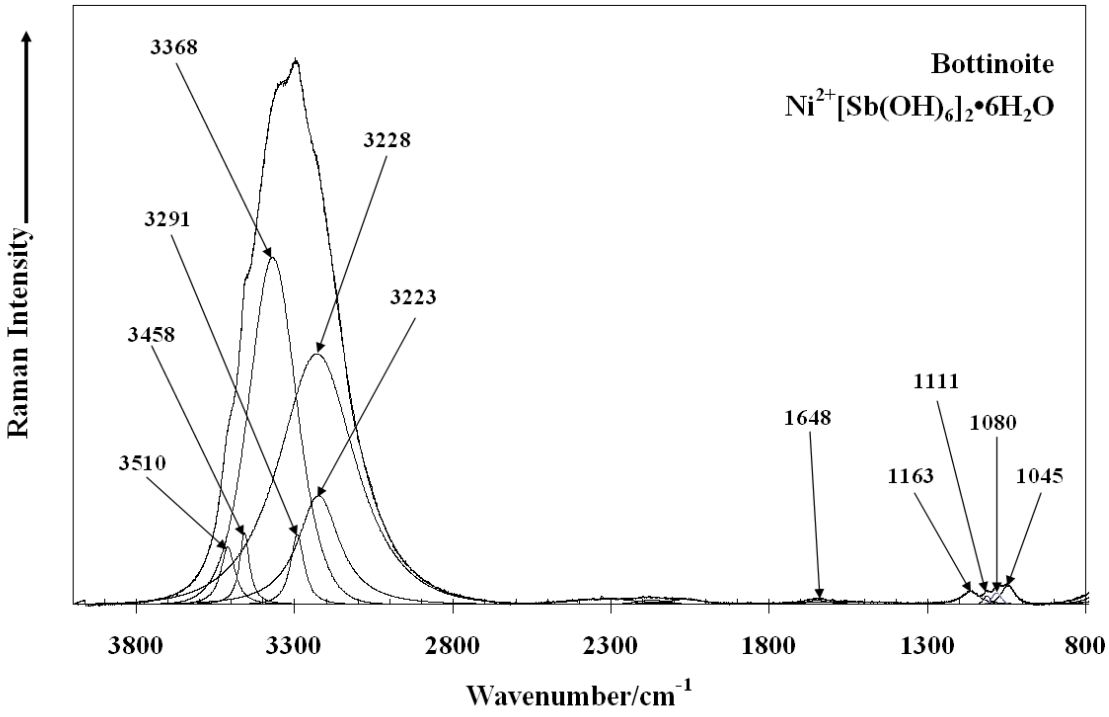

Bottinoite
$Ni^{2+}[Sb(OH)_6]_2 \cdot 6H_2O$
Raman Intensity
336
302
317
361
235
254
207
146
114
125
169
400
350
300
250
200
150
100
Wavenumber/cm^{-1}

Fig. 2



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280

281 **Fig. 3**

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